| OF |
AD
A070777

END
DATE
FILMED

8 - 79
DDC
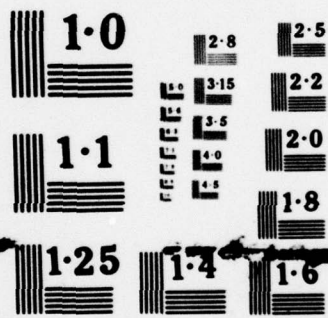
LEVEL

(12)

Linked and Mercury-Bridged Nido-Carboranes. High-Yield Synthesis of $\mu,\mu'-[(CH_3)_2C_2B_4H_5]_2Hg$, Conversion to $5,5'-[(CH_3)_2C_2B_4H_5]_2$, Cleavage, and Oxidative Addition of Benzene. Synthesis of $\mu,\mu'-(B_5H_8)_2Hg$

Narayan S. Hosmane and Russell N. Grimes

Department of Chemistry, University of Virginia

Charlottesville, Virginia 22901

Prepared for Publication

in

Inorganic Chemistry

June, 1979

Technical rept.,

DDC
RECEIVED
JUL 2 1979
C

TR-29

DDC FILE COPY

Linked and Mercury-Bridged Nido-Carboranes. High-Yield

Synthesis of μ,μ'-[(CH$_3$)$_2$C$_2$B$_4$H$_5$]$_2$Hg, Conversion to 5,5'-

[(CH$_3$)$_2$C$_2$B$_4$H$_5$]$_2$, Cleavage, and Oxidative Addition of

Benzene. Synthesis of μ,μ'-(B$_5$H$_8$)$_2$Hg
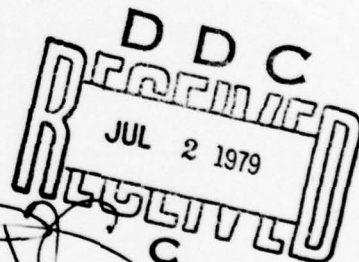
Narayan S. Hosmane and Russell N. Grimes*

Abstract. The nido-carborane anion [2,3-(CH$_3$)$_2$C$_2$B$_4$H$_5$]$^{(-)}$ reacts readily
with anhydrous HgCl$_2$ in THF at room temperature, producing the bis
(carboranyl) mercury(II) complex μ,μ'-[(CH$_3$)$_2$C$_2$B$_4$H$_5$]$_2$Hg in which the
metal is bound to two carborane ligands via B-Hg-B three-center, two-
electron bridge bonds. On heating at 180° deg in benzene, this compound
quantitatively expels free mercury and forms the B-B linked nido-
carborane 5,5'-[(CH$_3$)$_2$C$_2$B$_4$H$_5$]$_2$ as a single pure isomer. Air oxidation
of the linked carborane in benzene solution results in cleavage of the
carborane-carborane B-B bond and oxidative addition of benzene to give
4-C$_6$H$_5$-2,3-(CH$_3$)$_2$C$_2$B$_4$H$_5$, an apparently air-stable derivative of nido-
2,3-C$_2$B$_4$H$_8$. Similar treatment of the linked carborane in C$_6$D$_6$ gives
the corresponding hexadeuterated carborane product. The reaction of
B$_5$H$_8$$^-$ ion with HgCl$_2$ in THF produces μ,μ'-(B$_5$H$_8$)$_2$Hg, a stable solid in
which mercury is evidently bridge-bonded to two pentaborane ligands.

Introduction

The small nido-carborane $2,3$-$C_2B_4H_8$ and its substituted deriva-
tives are exceedingly versatile ligands which readily form η^1, η^2,
and η^5 complexes with metal and metalloid groups. Insertion of units
such as $(CO)_3Fe$ or $(\eta^5$-$C_5H_5)Co^{2+}$ into the open face of the pyramidal
species $R_2C_2B_4H_6$ (R = H,CH_3) or their anions $(R_2C_2B_4H_5^-)$ yields closo-
metallocarboranes in which the metal is η^5-bonded to the carborane and
completes a 7-vertex MC_2B_4 polyhedral cage system. A rather extensive
chemistry has been developed in this area[1] including the oxidative
fusion of face-bonded C_2B_4 ligands coordinated to the same metal ion to
give tetracarbon C_4B_8 cages. In contrast, the attack of mono-coordinate
units such as $(\eta^5$-$C_5H_5)Fe(CO)_2^+$, $[(C_6H_5)_3P]_3Rh^+$, $[(C_6H_5)_3P]Au^+$, and
$R_3M_{IV}^+$ (R = H,CH_3; M_{IV} = Si,Ge,Sn,Pb) on the $R_2C_2B_4H_5^-$ ion generates
<u>bridge</u>-substituted complexes in which the metal is η^2-linked to the
edge of the carborane cage by a three-center B-M-B bond.[2f] In some
cases these bridged species undergo thermal rearrangement to terminally
(η^1)-substituted isomers.[2]

If an $R_2C_2B_4H_5^-$ substrate is allowed to interact with a <u>di</u>-
coordinate metal or metalloid group, one expects to form <u>bis</u>-carborane
complexes in which the metal participates in B-M-B three-center bonds
on two <u>different</u> cages. The only reported example is μ,μ'-$SiH_2(C_2B_4H_7)_2$,
prepared in this laboratory several years ago.[2d] We are currently
interested in doubly bridged complexes, in part because of their potential
utility as precursors to linked nido-carboranes. These, in turn, open new

mass spectrum displays an intense parent grouping (cutoff at m/e 410) and strong groups with local cutoffs at m/e 307, 204, and 104 which correspond to the fragments $[(CH_3)_2C_2B_4H_5]Hg^+$, Hg^+, and $(CH_3)_2C_2B_4H_6^+$, respectively; in each case the pattern of intensities is consistent with the composition indicated, based on natural isotope distributions of boron and mercury.

The 32.1-MHz ^{11}B NMR spectrum (Figure 2) exhibits a high field symmetric doublet corresponding to the apex B-H, and an unsymmetric doublet at lower field assigned to overlapping B(4)-H, B(5)-H, and B(6)-H resonances; the chemical shifts (Table I) correspond closely to those of $2,3-(CH_3)_2C_2B_4H_6$ (δ -3.7, -7.2, and -47.7 ppm).[6] The proton NMR spectrum (Table II) reveals two nonequivalent methyl environments and confirms the presence of bridging hydrogens, as shown by a broad, weak peak in the B-H-B region.

The location of mercury in a bridging, rather than a terminal position, on the cage can be inferred from the absence of a separate ^{11}B-Hg singlet in the undecoupled ^{11}B spectrum; terminal substitution on boron would be expected to produce collapse of the ^{11}B-H doublet to a singlet, and a shift with respect to the unsubstituted boron resonance. Further support for the bridged structure is found in the infrared spectrum (Table III) which contains a split B-H stretching band near 2500 cm^{-1}, a feature exhibited by all known heteratom-bridged $C_2B_4H_8$ derivatives, but which is absent in terminally-substituted species.[2]

Two isomeric arrangements are possible in I, one having C_s symmetry and the other C_2. The NMR spectra give no indication of the presence of more than one isomer (which is not surprising since one

would expect any differences in chemical shifts to be minute) and it is not possible to distinguish between the C_s and C_2 structures from available data. Indeed, it is probable that both isomers form in the reaction, since with the presumed linear (sp) hybridization of mercury the stereochemical preference for one arrangement over the other would be small. This problem is reminiscent of the question of structure in $\mu,\mu'-(C_2B_4H_7)_2SiH_2$ as discussed several years ago.[2d] In the silicon system, there was some indication, based on $^1\underline{H}$-Si NMR resonances, that the formation of the C_s isomer was favored (though both the C_s and the C_2 isomers form) in the reaction of $C_2B_4H_7^-$ ion with SiH_2Cl_2. Evidently the tetrahedral hybridization on silicon, and the presence of silyl hydrogens, produce significant steric interaction between the carborane ligands and thereby lead to inequality in the amounts of the two isomers formed. This is unlikely to be the case in I.

Compound I is the first confirmed example of a μ-carboranyl mercury complex, although we have reported the preparation of $\mu-(C_6H_5Hg)-C_2B_4H_7$ as a partially characterized species which decomposed in air to release elemental mercury.[2f] Several mercury complexes of the $B_{10}H_{12}^{2-}$ ligand are known in which the metal is coordinated to one or two of the decaborane units; the mercury-borane linkages are probably η^4, but bridged (η^2) structures have not been eliminated.[7] A number of σ-carboranyl mercury complexes are known, all of them derived from the icosahedral 1,2-, 1,7-, or $1,12-C_2B_{10}H_{12}$ carboranes.[8] Most of these species involve Hg-C links, although a few examples of mercury substitution at boron in $C_2B_{10}H_{12}$ species have been reported.[8b-d]

Synthesis of $5,5'-[(CH_3)_2C_2B_4H_5]_2$. The mercury-bridged complex
I at 180° in benzene expels mercury as the free metal and forms the
biscarborane $5,5'-[(CH_3)_2C_2B_4H_5]_2$ (II) in 91% yield (Figure 1). In
addition to bulk experiments conducted on a 1-2 gram scale, this
conversion was monitored via proton NMR over an 18-hr period, and was
observed to occur cleanly and quantitatively with no indications of the
presence of intermediate species. Moreover, only one isomer (II) is
formed insofar as can be detected.

The product II is a colorless liquid that can be distilled in
vacuo at 70°. The ^{11}B, ^1H, and ^{13}C NMR spectra indicate high (C_{2v}) symmetry
with only one C-CH$_3$ environment and two boron signals in a 3:1 area ratio.
The area-3 ^{11}B resonance (Figure 3) consists of a doublet of doublets
arising from the equivalent B(4,6)-H groups in each cage, superimposed
on the B(5)-B(5') singlet. The secondary splitting of the large doublet
is due to coupling between the terminal protons on B(4,6) and B(4',6')
and adjacent B-H-B bridging protons. The presence of the B(5)-B(5')
singlet can be deduced from the slight asymmetry of the superimposed
doublet and of the proton-decoupled (collapsed) peak in Figure 3B.
Although equivalence of the four methyl groups could be produced by
linkage either at B(5)-B(5') or at B(1)-B(1'), the latter possibility
is eliminated by the fact that the apical boron resonance (which
characteristically appears at high field in pyramidal boranes and
carboranes[9]) is a doublet, showing that the apex borons retain their
terminal hydrogens. In addition, of course, B(5)-B(5') linkage is
much more easily reconciled with the synthesis from the bridged complex.
The conversion of I to II with elimination of mercury is reminiscent
of the formation of $(CH_3)_3Si-SiH_3$ from $(CH_3)_3Si-Hg-SiH_3$ at room tempera-
ture.[10]

Compound II is the first pure isomer of a small linked nido-carborane to be isolated, although as mentioned above a mixture of $[(CH_3)_2C_2B_4H_5]_2$ isomers has been obtained by photolysis of $(CH_3)_2C_2B_4H_6$ in the presence of mercury. The only other example of a bis (nido-carborane) system to our knowledge is $(1,2-C_2B_9H_{11})_2$, which consists of linked icosahedral-fragment moieties and was produced by oxidative coupling of $C_2B_9H_{12}^-$ anions with K_2CrO_4.[11]

Cleavage of 5,5'-$[(CH_3)_2C_2B_4H_5]_2$ and Oxidative Addition of Benzene. The linked carborane (II) is exceedingly air-sensitive, and in the absence of solvent reacts instantly with atmospheric oxygen at room temperature to produce a novolatile white solid that is insoluble in organic solvents. However, exposure to air of a solution of II in benzene gave remarkably different results, rapidly generating the 4-phenyl derivative of the monomeric carborane in nearly quantitative yield (Figure 4).

$$1/2\ 5,5-[(CH_3)_2C_2B_4H_5]_2\ +\ \ C_6H_6\ \xrightarrow[-2H]{O_2}\ \ 4-C_6H_5-2,3-(CH_3)_2C_2B_4H_5\ (III)$$
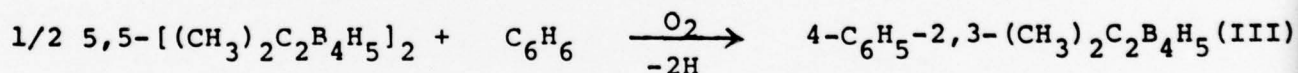
The oxygenated product may be water, although this was not established.

Structural characterization of III, a colorless oil, was straight-forward (Tables I-III); phenyl substitution obviously occurs at B(4), since the ^{11}B NMR (Figure 5) and proton NMR indicate low symmetry. When this reaction was conducted in benzene-d_6, the mass spectrum of the product indicated a hexadeuterated species corresponding to $C_6D_5-(CH_3)_2C_2B_4H_4D$, indicating that all six hydrogens of benzene are retained in the product. Thus we formulate the reaction as an oxidative

addition of benzene to $(CH_3)_2C_2B_4H_5-H_5B_4C_2(CH_3)_2$ with concomitant cleavage of the central B-B link. As shown, one hydrogen from benzene is proposed to enter a bridging position, replacing a bridge hydrogen which moves to a terminal location on B(5). The phenyl dimethyl carborane, III, appears to be reasonably air-stable and does not decompose noticeably on handling in air over periods of a few hours. This property, combined with its low volatility and ready availability via the sequence described here, makes III a good candidate for extensive bench chemistry including the synthesis of metallocarborane derivatives.

As a control experiment, a solution of II in cyclohexane was exposed to the atmosphere and was found to undergo only slow decomposition to insoluble white solids; in contrast to the oxidation in benzene, no substituted carboranes were detected.

<u>Synthesis of $\mu,\mu'-(B_5H_8)_2Hg$ (IV)</u>. The ease with which the bis(carboranyl)mercury complex I forms from $(CH_3)_2C_2B_4H_5^-$ and $HgCl_2$, led us to examine the analogous reaction of the $B_5H_8^-$ ion. The $-30^\circ C$ addition of $HgCl_2$ to a THF solution of NaB_5H_8 gave white, crystalline, sublimable $\mu,\mu'-[B_5H_8]_2Hg$ in nearly quantitative yield. The mass spectrum exhibits strong groupings with local cutoffs at m/e 330 (parent peak), 267, and 204, corresponding to $(B_5H_8)_2Hg^+$, $(B_5H_8)Hg^+$, and Hg^+, respectively. The ^{11}B NMR spectrum (Figure 6) contains an apex B-H doublet which collapses to a singlet on proton decoupling, indicating that mercury attachment to the boron cage occurs at a basal, not apical position; moreover, the presence of only one apex B-H resonance implies a symmetrical structure in which both B_5H_8

ligands are bound to the metal in identical fashion. The only such arrangements are μ,μ'- and $2,2'$-$(B_5H_8)_2$Hg, and from NMR data the μ,μ'-structure can be assigned. The near-superposition of the ^{11}B resonances of the basal boron atoms is more consistent with bridge than terminal substitution; 32-MHz ^{11}B spectra of 2-metallated B_5H_9 derivatives usually exhibit clear nonequivalence of the basal borons.[12] The ^{11}B-decoupled ^{1}H spectrum has superimposed basal $H_{terminal}$ peaks, but the base-apex-bridge area ratio of 4:1:3 conforms with the bridged structure, as does the obser-vation of strong ^{199}Hg-^{1}H$_{terminal}$ coupling (Table II).

A number of bridged pentaborane complexes have been reported by Gaines and coworkers,[12a,c] notably the μ-$(R_3M)B_5H_8$ series in which M is Si, Ge, Sn, or Pb and R is H or alkyl. The compound $[C_6H_5)_3P]_2\bigcirc$ CuB_5H_8, prepared by Brice and Shore,[13] has been shown to have a B-Cu-B bridge, as confirmed in an X-ray diffraction study.[14] Several bis(pentaboranyl) species of the type $(B_5H_8)_2MRR'$ [M = Si, Ge; R = H, CH_3] are also known,[12c] and these have been assigned $\mu,2'$ or $2,2'$ structures. However, bis(pentaboranyl) complexes of the μ,μ' type have not, to our knowledge, been described prior to this work, nor have mercury-substituted pentaborane derivatives of any structural class been reported previously.

The possibility that IV may serve as an efficient precursor to a linked $(B_5H_8)_2$ species (whose three possible isomers have been obtained by other methods[15]), was not extensively studied, but pyrolysis of IV at $70°$ for 20 hr gave B_5H_9, a small quantity of $(B_5H_8)_2$ (detected mass spectroscopically), elemental mercury, and nonvolatile solids.

Summary

The development of a simple high-yield route to linked nido-carboranes is of practical significance, since the linked compounds can serve as precursors to a variety of novel heterocarboranes, metallocarboranes, and tetracarbon carboranes. Indeed, this was the main rationale for initiation of this work. However, the unexpected observation of oxidative addition of benzene to the linked carborane opens up additional synthetic possibilities, particularly if such reactions prove to be general. We know of no precedent for oxidative addition of arenes to carboranes, and it is tempting to speculate that this process initially involves oxygen-promoted homolytic cleavage of the biscarborane to generate $(CH_3)_2C_2B_4H_5\cdot$ radicals which in turn combine with the solvent. Studies of the oxidation of $5,5'-[(CH_3)_2C_2B_4H_5]_2$ and similar linked carboranes in other solvents will be required to test this point.

Experimental Section

Materials. 2,3-dimethyl-2,3-nido-dicarbahexaborane(8),
2,3-$(CH_3)_2C_2B_4H_6$, was prepared by reaction of 2-butyne with penta-
borane(9) in the presence of triethylamine   as described elsewhere.[16]
All other reagents were commerically obtained and used as received.

Spectra. Boron-11 and proton pulse Fourier transform NMR spectra
at 32.1 and 100 MHz, respectively, were recorded on a JEOL PS-100P
spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer
system. Unit-resolution mass spectra were obtained on a Hitachi
Perkin-Elmer RMU-6E mass spectrometer, while high-resolution mass
measurements were conducted on an AEI MS-902 double-focusing instru-
ment equipped with an SRI chemical ionization source. All high-
resolution spectra were recorded under chemical ionizing conditions
in methane or argon-water. Infrared spectra were obtained on a
Beckman IR-8 instrument.

Preparation of [2,3-$(CH_3)_2C_2B_4H_5]_2$Hg (I). $Na^+(CH_3)_2C_2B_4H_5^-$
(prepared by reaction of 5.94 mmol of 2,3-$(CH_3)_2C_2B_4H_6$ with excess
sodium hydride in THF as described previously[5]) was dissolved in
30 ml of dry THF and 3.00 mmol of anhydrous $HgCl_2$ was added on the
vacuum line. After stirring the mixture for 4 hr at $25^{\circ}C$, during
which a white precipitate formed, 30 ml hexane was added under a dry
N_2 atomosphere. The solution was filtered through sintered glass
and the solvent was removed by vacuum distillation. The residue was
heated at 70° in a sublimator under vacuum, and white crystalline I
condensed on the cold finger which was maintained at -78°. The yield
of I was 1.050 g (2.58 mmol, 87% based on starting carborane). Exact
mass measurement: calcd. for $^{202}Hg^{12}C_8^{11}B_8^{1}H_{22}^+$ 408.2172, found 480.2176.
^{13}C NMR in C_6D_6: sharp CH_3 peaks of equal area at δ 18.0 and 19.2 ppm rel. to TMS.

Conversion of I to [2,3-$(CH_3)_2C_2B_4H_5]_2$ (II). A 1.31-g sample
(3.21 mmol) of [$(CH_3)_2C_2B_4H_5]_2$Hg was placed under N_2 in a 30-ml
Pyrex ampoule fitted with a break-seal, 5 ml of dry benzene was
added, the contents were frozen in liquid nitrogen, and the ampoule
was sealed under vacuum. The mixture was heated at 180° for 18 hr,
during which the originally colorless solution acquired a pale
brown color and mercury globules collected at the bottom. During
this period a parallel experiment was conducted on a smaller sample
in a sealed Pyrex 5 mm NMR tube which was heated at 180° for 18 hr
with periodic monitoring of the 100-MHz ^{1}H NMR spectrum; in this
way it was ascertained that the reaction reached completion with
complete disappearance of the original spectrum.

The ampoule was opened under vacuum, filtered under vacuum into
a 50 ml flask, and the mercury which remained on the filter was
washed with hexane, dried, and weighed; the yield was 0.66 g (3.26
mmol), corresponding to slightly greater than theoretical yield.
The filtrate was stripped of solvent and the liquid residue was
distilled at 70° under vacuum into a trap cooled to 0°C, to give
0.60 g (2.91 mmol, 91% yield) of colorless liquid 5,5'-[2,3-$(CH_3)_2C_2B_4H_5]_2$
(II). Exact mass: calcd for $^{12}C_8{}^{11}B_8{}^1H_{22}{}^+$ 206.2466, found 206.2477.
^{13}C NMR in C_6D_6: sharp CH_3 peak at δ 21.0 ppm rel. to TMS.
Oxidation of [2,3-$(CH_3)_2C_2B_4H_5]_2$ in Benzene. A 100-mg (0.48 mmol)
sample of 5,5'-[$(CH_3)_2C_2B_4H_5]_2$ (II) was dissolved in 5.0 ml of dry
benzene and this solution was shaken in air for 5 min, during which
a small amount of white precipitate formed. The solution was filtered
in air and the solvent was removed by distillation in vacuum at 25°,
which was continued for 2 hr to remove the last traces of volatiles.

The residue consisted of colorless, viscous $4-C_6H_5-2,3-(CH_3)_2C_2B_4H_5$ (III) which was purified by distillation at 78 °C into a U-trap at 0°C:
yield 0.163 g (0.905 mmol, 94 %). Exact mass: calcd for $^{12}C_{10}{}^{11}B_4{}^1H_{17}{}^+$ (protonated parent ion) 181.1703, found 181.1712.

Synthesis of $\mu,\mu'-(B_5H_8)_2Hg$ (IV). A THF solution of $Na^+B_5H_8{}^-$ was prepared from 0.648 g (10.1 mmol) of B_5H_9 and 0.553 g (23.0 mmol) NaH in 50 ml THF, and filtered in vacuo onto 1.32 g (4.82 mmol) of anhydrous $HgCl_2$ in a 250-mL round-bottom flask cooled to -78°C. The solution was warmed to -30°C and stirred for 2 hr with little or no evolution of gas. After distillation of solvent out of the mixture at -30°C over a 2-hr period a gray residue remained. To this residue 50 mL of dry hexane was added, the solution was filtered in vacuo, solvent was returned to the flask containing the reaction residue, and the solution was filtered again. This process was repeated several times in order to extract most of the $(B_5H_8)_2Hg$, which is not highly soluble in hexane or other organic solvents. Evaporation of the solvent followed by sublimation of the product at 100° for 8 hr gave 1.67 g (5.08 mmol, 90% yield) of pure white crystalline $(B_5H_8)_2Hg$, mp. 161-162° (sealed capillary). The compound is moderately air-stable, surviving exposure of several hr in the solid state without noticeable decomposition.

Pyrolysis of IV. A 0.656 g (2.0 mmol) sample of IV was placed in an evacuated Pyrex tube and heated for 20 h at 70°C, after which the volatile products were fractionated through traps at -63 and -196°C. The -196° fraction was nearly pure B_5H_9 (ir and mass spectra), 2.68 mmol. The -63° condensate was shown by mass spectroscopic analysis to consist of B_5H_9 and a small quantity of $(B_5H_8)_2$, isomer not identified.

-14-

References and Notes

(1) Review: Grimes, R. N., in "Organometallic Reactions and Syntheses", Vol. 6,   Becker, E. I. and Tsutsui, M., Ed., Plenum, New York, N.Y., 1977, Chapter 2.

(2) (a) Thompson, M. L., and Grimes, R. N., _Inorg. Chem._, _1972_, _11_, 1925; (b) Savory, C. G., Wallbridge, M. G. H., _Chem. Commun._, _1971_, 622; (c) Savory, C. G.; Wallbridge, M. G. H., _J. Chem. Soc., Dalton Trans._, _1972_, 918; (d) Tabereaux, A.; Grimes, R. N., _Inorg. Chem._, _1973_, _12_, 792; (e) Sneddon, L. G.; Beer, D. C.; Grimes, R. N., _J. Am. Chem. Soc._, _1973_, _95_, 6623; (f) Magee, C. P.; Sneddon, L. G.; Beer, D. C; and Grimes, R. N., _J. Organometal. Chem._, _1975_, _86_, 159.

(3) Plotkin, J. S.; Astheimer, R. J.; and Sneddon, L. G., _J. Am. Chem. Soc._, in press.

(4) Grimes, R. N., _Acc. Chem. Res._, _1978_, _11_, 420.

(5) Onak, T. and Dunks, G. B., _Inorg. Chem._, _1966_, _5_, 439.

(6) Onak, T. P.; Williams, R. E.; and Weiss, H. G., _J. Am. Chem. Soc._, _1962_, _84_, 2830.

(7) (a) Greenwood, N. N.; Thomas, B. S.; and Waite, D. W., _J. Chem. Soc., Dalton Trans._, _1975_, 299; (b) Greenwood, N. N. and Sharrocks, D. N., _J. Chem. Soc._ (A), _1969_, 2334; (c) Greenwood, N. N. and Ward, I. M., _Chem. Soc. Rev._, _1974_, _3_, 231; (d) Greenwood, N. N., _Pure and Applied Chem._, _1977_, _49_, 791.

(8) (a) A number of older references are given by Grimes, R. N.,

"Carboranes", Academic Press, N.Y., 1970; see also (b)

Bregadze, V. I.; Kampel, V. Ts.; and Godovikov, N. N.,

J. Organometal. Chem., 1976, 112, 249; (c) Bregadze, V. I.;

Kampel, V. Ts.; and Godovikov, N. N., Izv. Akad. Nauk SSSR,

Ser. Khim., 1977, 1630, and (d) Kampel, V. Ts.; Butin, K. P.;

Bregadze, V. I.; and Godovikov, N. N., ibid., 1978, 1508.

(9) Eaton, G. R., and Lipscomb, W. N., "NMR Studies of Boron

Hydrides and Related Compounds", Benjamin, New York, 1969.

(10) Cradock, S.; Ebsworth, E. A. V.; Hosmane, Narayan S.; Mackay,

K. M., Angew. Chem. Internat. Edit. Engl., 1975, 14, 167.

(11) Janousek, Z.; Hermanek, S.; Plesek, J.; Stibr, B., Coll. Czech.

Chem. Commun., 1974, 39, 2363.

(12) (a) Gaines, D.F. and Iorns, T.V., J. Am. Chem. Soc., 1968, 90, 6617;

(b) Gaines, D.F. and Iorns, T.V., Inorg. Chem., 1968, 7, 1041;

(c) Gaines, D.F., and Ulman, J., ibid., 1974, 13, 2792.

(13) Brice, V.T. and Shore, S.G., J. Chem Soc., Dalton Trans, 1975, 334.

(14) Greenwood, N.N.; Howard, J.A.; McDonald, W.S., J. Chem. Soc.,

Dalton Trans., 1977, 37.

(15) (a) Grimes, R. N.; Wong, F. E.; Lewin, R.; and Lipscomb, W. N.,

Proc. Nat. Acad. Sci., U.S., 1961, 47, 996; (b) Gaines, D. F.;

Iorns, T. V.; and Clevenger, E. M., Inorg. Chem., 1971, 10, 1096;

(c) Plotkin, J. S., and Sneddon, L. G., J. Chem. Soc., Chem.

Commun., 1976, 95.

(16) N. S. Hosmane and R. N. Grimes, submitted for publication.

Table I. 32.1-MHz ^{11}B FT NMR Data

Compound	Solvent	δ, ppm[a] (J,Hz)	Relative areas
μ,μ'-[$(CH_3)_2C_2B_4H_5]_2$Hg (I)	CDCl$_3$	-4.0(117)	3
		-47.7(181)	1
5,5'-[$(CH_3)_2C_2B_4H_5]_2$ (II)	C$_6$D$_6$	-3.33(151)[b], (44)[c]	3[d]
		-46.25(166)	1
4-C$_6$H$_5$-2,3-$(CH_3)_2$-2,3-C$_2$B$_4$H$_5$ (III)	CDCl$_3$	+5.89[e], -2.18($\sim$180)[f], -4.92(180)[f], -44.8(176)	1,1,1,1
μ,μ'-(B$_5$H$_8$)$_2$Hg (IV)	C$_6$D$_6$	[-7.92, -9.60],[g]	3
		-43.85(176)	1

[a]Chemical shifts relative to BF$_3$·O(C$_2$H$_5$)$_2$ with positive sign denoting downfield shift. [b]Primary splitting (151 Hz) assigned to H$_{terminal}$ (4,6)-^{11}B coupling. [c]Secondary splitting (44 Hz) assigned to H$_{bridge}$-^{11}B coupling. [d]Area-3 peak consists of superimposed resonances arising from B(4,6) and B(5). [e]Singlet arising from ^{11}B(4)-C$_6$H$_5$. [f]Heavily overlapped doublets which collapse to singlets in the ^{1}H-decoupled spectrum. [g]Nearly superimposed resonances (apparent doublets) which collapse to overlapping singlets in the ^{1}H-decoupled spectrum.

Table II.   100-MHz ^{1}H FT NMR Data (C_6D_6 Solution)

Compound	δ,ppm (rel area)[a]	Assignment
μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$ (I)	1.90(1)[b], 1.94(1)[b]	CH_3, CH_3
	$\sim$ -2.3[c]	B-H-B
5,5'-$[(CH_3)_2C_2B_4H_5]_2$ (II)	1.80(6)	CH_3
	3.37[d] ($\sim$2)	H_t (base)
	-0.70[e] ($\sim$1)	H_t (apex)
	$\sim$ -2.0[c]	B-H-B
4-C_6H_5-2,3-$(CH_3)_2C_2B_4H_5$ (III)	2.10(1), 2.00(1)	CH_3, CH_3
	4.90[f]	H_t (base)
	-0.60[g]	H_t (apex)
	-1.70[c]	B-H-B
	7.25[h]	C_6H_5
μ, μ'-$(B_5H_8)_2Hg$ (IV)	2.39(4)[j,k]	H_t (base)
	-1.82(1)[j,m]	H_t (apex)
	-2.90(3)[j,m,n]	B-H-B

[a]Chemical shifts relative to $(CH_3)_4Si$ with positive sign indicating downfield shift. [b]Satellites due to ^{199}Hg-^{1}H coupling (J = 39 Hz) are visible near the methyl resonances; these peaks are unaffected 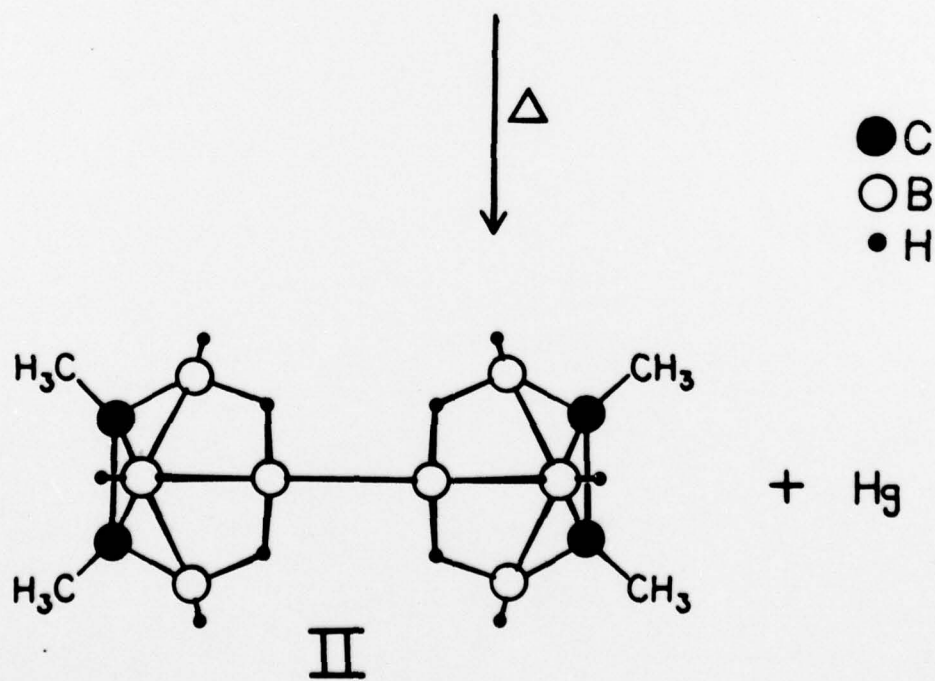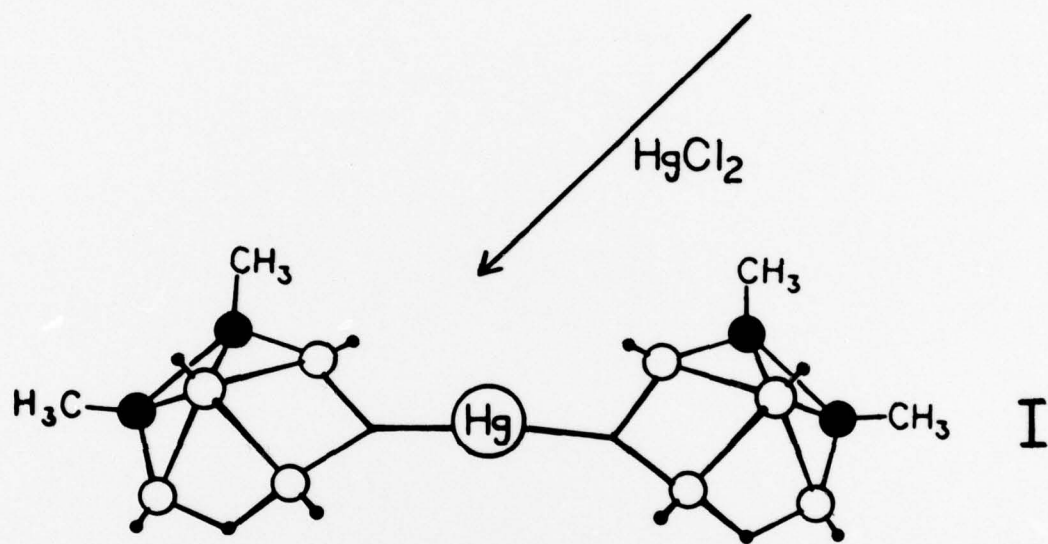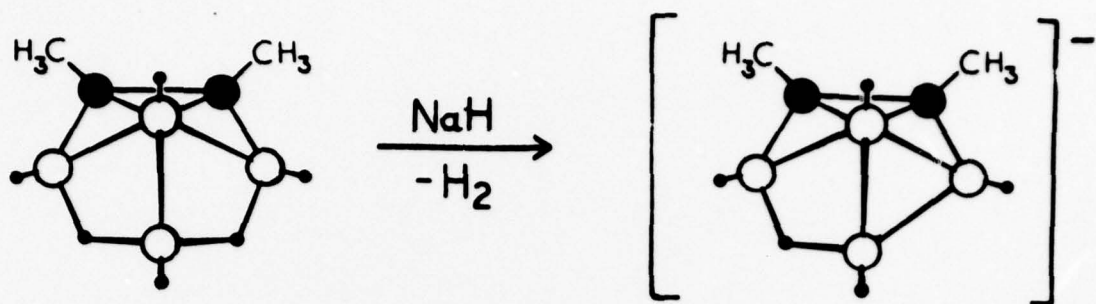by sample spinning, and disappear on conversion of I to II. [c]Broad peak, area not measurable. [d]Quartet, J = 158 Hz. [e]Quartet, J = 180 Hz. [f]Quartet, J = 165 Hz. [g]Quartet, J = 180 Hz. [h]Multiplet. [j]Singlet observed on ^{11}B-decoupling. [k]Satellites due to ^{199}Hg-^{1}H(base) coupling are observed with J = 141 Hz. [m]Line-narrowing produced fine structure due to H-H coupling with J $\approx$ 10 Hz. [n]Satellites due to ^{199}Hg-^{1}H(bridge) coupling are observed with J = 96 Hz.
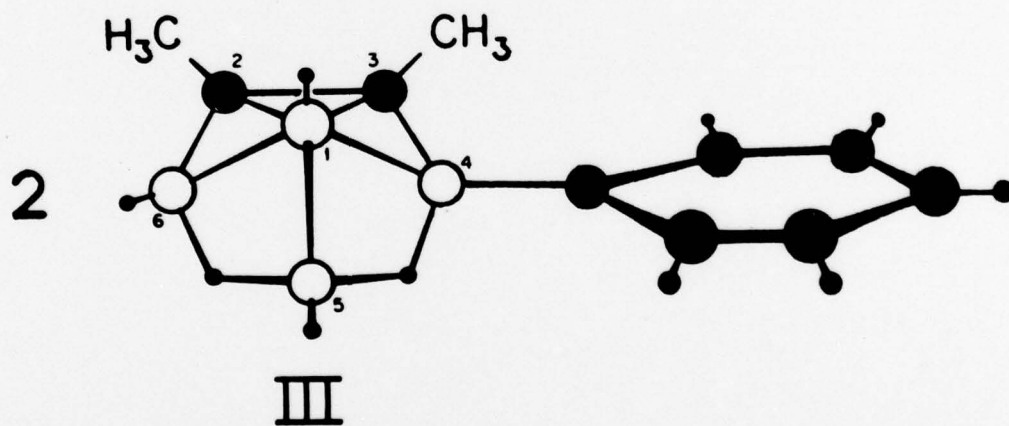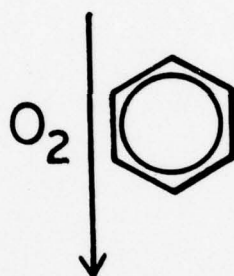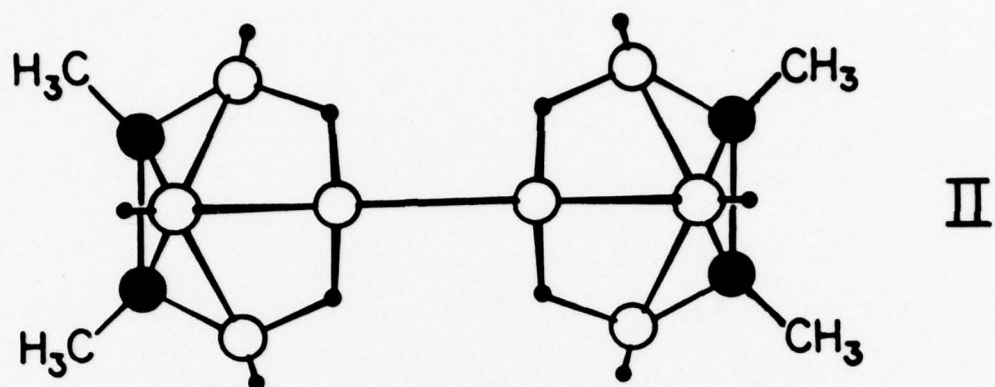
Table III.   Infrared Absorptions, cm^{-1} (CCl_4 vs. CCl_4).

I

2970 m, 2942 m, 2915 s, 2855 s, 2570 vs, br, 2490 s,
1900 m,br, 1810 m, 1540 sh, 1495 s, 1435 s, 1365 s,
1330 sh, 1250 m, 1210 w, 1150 s, 1090 m, 1000 sh,
985 s, 960 s, 910 m, 895 w, 860 s, 800 s, v br, 720 s,
675 s, 625 s.

II

3070 m, 3050 m, 3000 w, 2980 sh, 2950 vs, 2920 vs,
2860 s, 2580 vs, 1930 m,br, 1885 m,br, 1435 vs,br,
1370 m, 1320 m,br, 1250 m,br, 1200 m, 110 m, 1060 m,
995 m, 933 m, 695 vs, 650 m.

III

3070 m, 3050 m, 2930 vs,br, 2860 sh, 2590 vs, 1930 m,br,
1890 m,br, 1410 vs, v br, 1330 vs,v br, 1205 m,br,
1110 w, 1055 s, 1000 w, 960 w, 935 w, 697 s, 650 s.

IV

2600 s, 2550 m, 1805 m,br, 1600 w, v br,]455 s, v br,
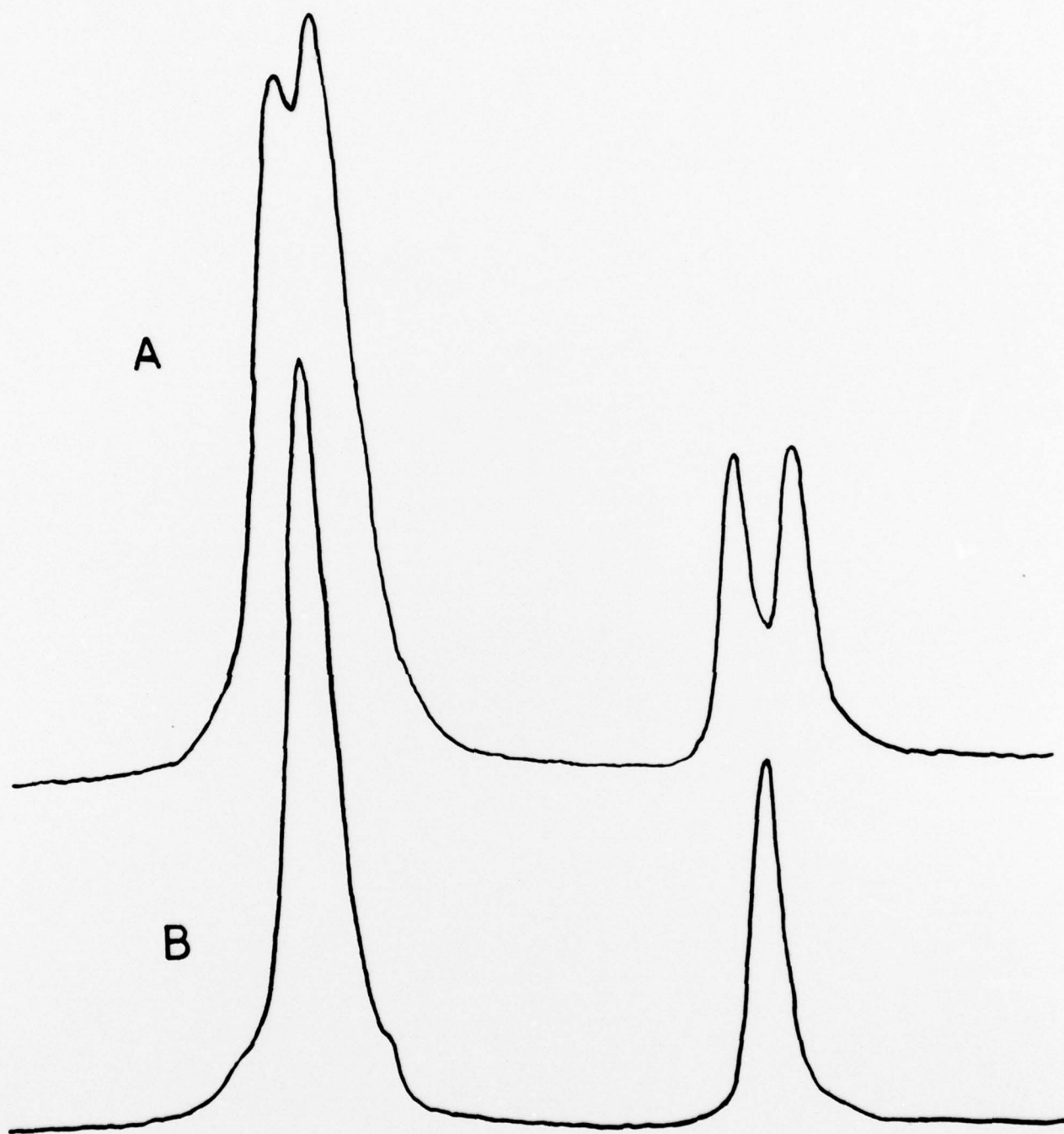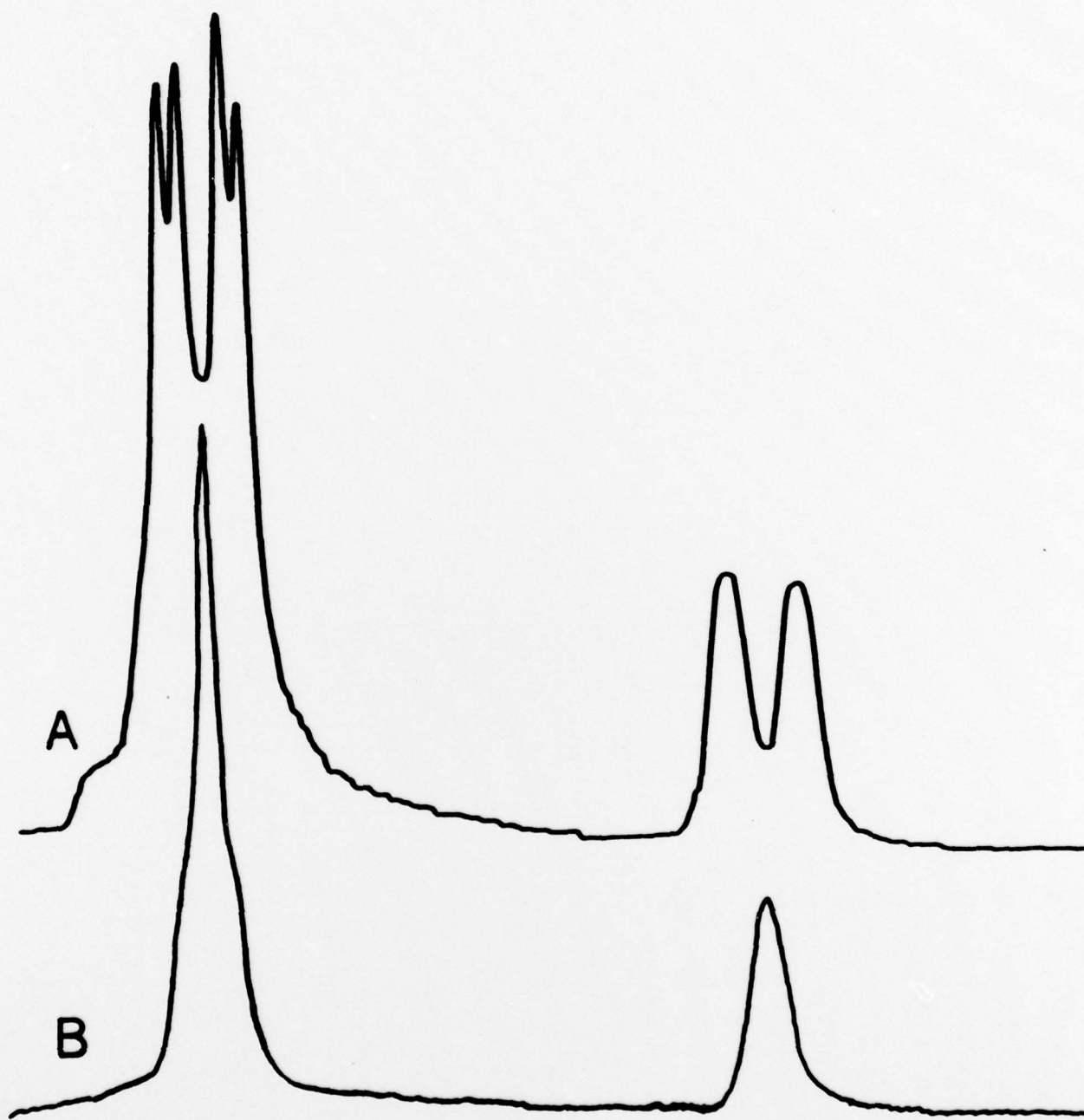1375 m, br, 1190 s, 1000 w, 930 m, 880 m, 715 m, br.

Figure Captions

Figure 1. Scheme for the formation of $\mu,\mu'-[(CH_3)_2C_2B_4H_5]_2Hg$ (I) and
its thermal conversion to $5,5'-[(CH_3)_2C_2B_4H_5]_2$ (II). Only
the isomer of I having C_s symmetry is shown; the product is
presumably a mixture of the C_s and C_2 isomers. In both
isomers, free rotation of carboranyl groups around the $Hg-B_2$
axis is assumed.

Figure 2. 32.1-MHz ^{11}B FT NMR spectra of $\mu,\mu'-[(CH_3)_2C_2B_4H_5]_2Hg$ (I)
in $CDCl_3$. A, undecoupled; B, proton-decoupled at 99.998404
Hz. Chemical shifts and coupling constants are reported in
Table I.

Figure 3. 32.1-MHz ^{11}B FT NMR spectra of $5,5'-[(CH_3)_2C_2B_4H_5]_2$ (II) in
C_6D_6. A, undecoupled; B, proton-decoupled.

Figure 4. Scheme showing the oxidative addition of benzene to II to
give $4-C_6H_5-2,3-(CH_3)_2C_2B_4H_5$ (III).

Figure 5. 32.1-MHz ^{11}B FT NMR spectra of $4-C_6H_5-2,3-(CH_3)_2C_2B_4H_5$ (III).
A, undecoupled; B, proton-decoupled.

Figure 6. Proposed structure and ^{11}B FT NMR spectra of $\mu,\mu'-(B_5H_8)_2Hg$. A, undecoupled; B, proton-decoupled.
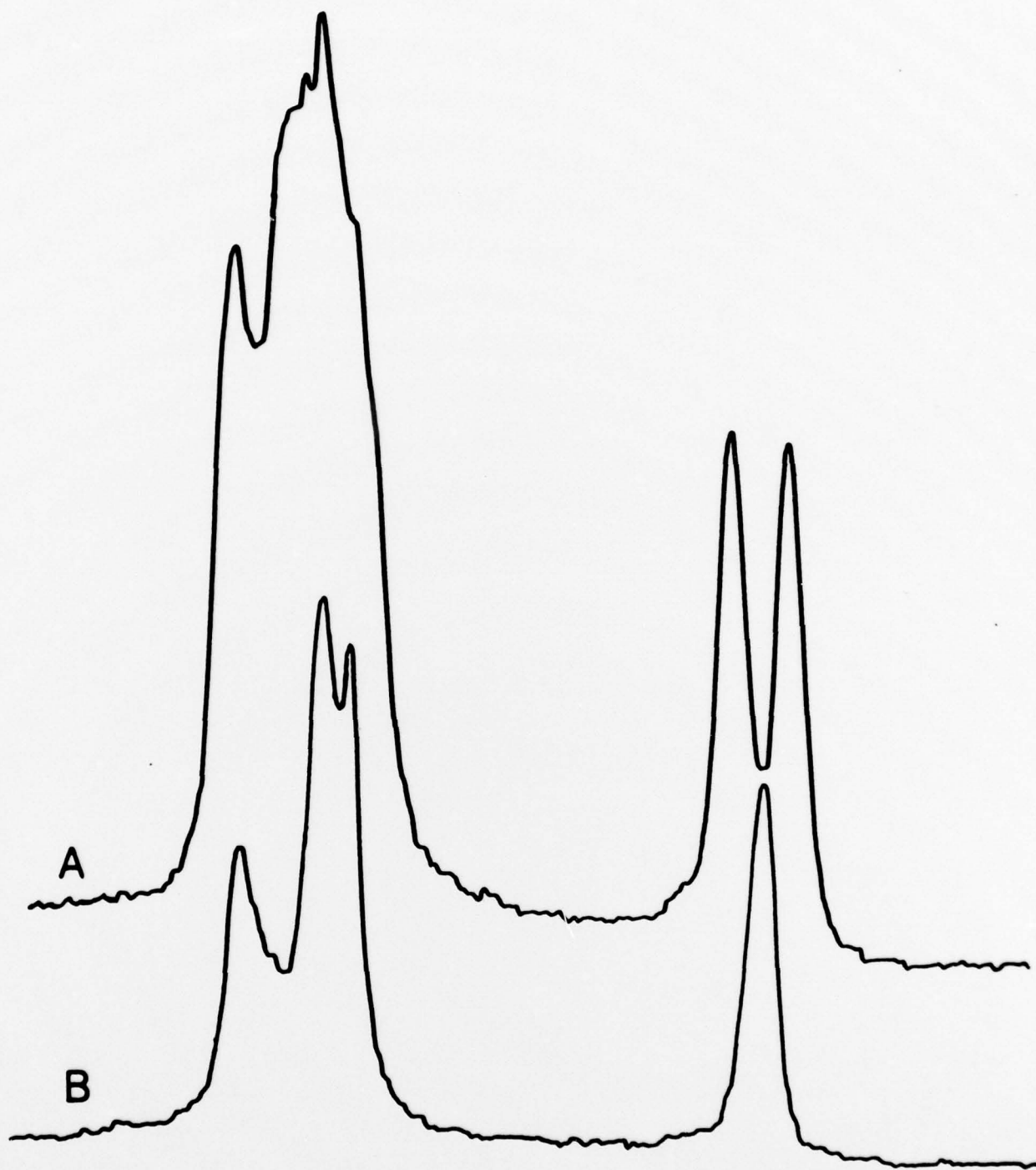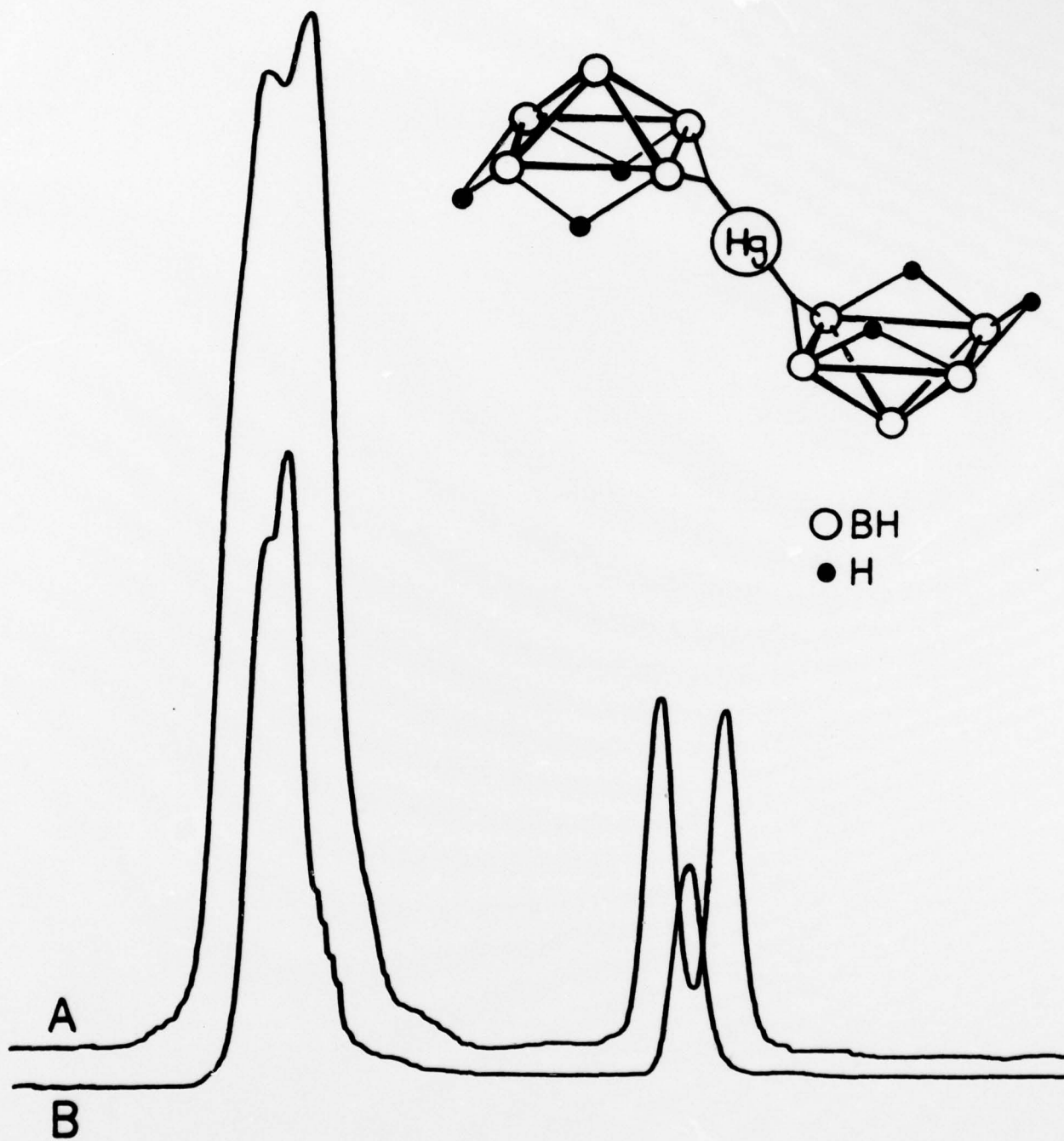
H₃C   CH₃   II

O₂

H₃C   CH₃

2   III

○ B   ● C   • H

O BH
● H

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 29	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Linked and Mercury-Bridged Nido-Carboranes. High-Yield Synthesis of μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$, Conversion to 5,5'-$[(CH_3)_2C_2B_4H_5]_2$, Cleavage, and Oxidative Addition of Benzene. Synthesis of μ,μ'-$(B_5H_8)_2Hg$		5. TYPE OF REPORT & PERIOD COVERED Interim
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Narayan S. Hosmane and Russell N. Grimes		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0305
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Virginia Department of Chemistry Charlottesville, Virginia 22901		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-569
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Branch, Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE June, 1979
		13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Carboranes	Bis(dicarbahexaboranyl)
Mercury	Bis(dicarbahexaboranyl)mercury(II)
Linked carboranes	Biscarboranes
Metal-bridged complexes	Bis(pentaboranyl)mercury(II)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

See page 1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217
Attn: Code 472   2

ONR Branch Office
536 S. Clark Street
Chicago, Illinois 60605
Attn: Dr. George Sandoz   1

ONR Branch Office
715 Broadway
New York, New York 10003
Attn: Scientific Dept.   1

ONR Branch Office
1030 East Green Street
Pasadena, California 91106
Attn: Dr. R. J. Marcus   1

ONR Area Office
One Hallidie Plaza, Suite 601
San Francisco, California 94102
Attn: Dr. P. A. Miller   1

ONR Branch Office
Building 114, Section D
666 Summer Street
Boston, Massachusetts 02210
Attn: Dr. L. H. Peebles   1

Director, Naval Research Laboratory
Washington, D.C. 20390
Attn: Code 6100   1

The Assistant Secretary of the Navy
    (R, E&S)
Department of the Navy
Room 4E736, Pentagon
Washington, D.C. 20350   1

Commander, Naval Air Systems Command
Department of the Navy
Washington, D.C. 20360
Attn: Code 310C (H. Rosenwasser) 1

Defense Documentation Center
Building 5, Cameron Station
Alexandria, Virginia 22314   12

U.S. Army Research Office
P.O. Box 1211
Research Triangle Park, N.C. 27709
Attn: CRD-AA-IP   1

Naval Ocean Systems Center
San Diego, California 92152
Attn: Mr. Joe McCartney   1

Naval Weapons Center
China Lake, California 93555
Attn: Dr. A. B. Amster
      Chemistry Division   1

Naval Civil Engineering Laboratory
Port Hueneme, California 93401
Attn: Dr. R. W. Drisko   1

Professor K. E. Woehler
Department of Physics & Chemistry
Naval Postgraduate School
Monterey, California 93940   1

Dr. A. L. Slafkosky
Scientific Advisor
Commandant of the Marine Corps
    (Code RD-1)
Washington, D.C. 20380   1

Office of Naval Research
800 N. Quincy Street
Arlington, Virginia 22217
Attn: Dr. Richard S. Miller   1

Naval Ship Research and Development
    Center
Annapolis, Maryland 21401
Attn: Dr. G. Bosmajian
      Applied Chemistry Division 1

Naval Ocean Systems Center
San Diego, California 91232
Attn: Dr. S. Yamamoto, Marine
      Sciences Division   1

	No. Copies		No. Copies
Dr. R. N. Grimes University of Virginia Department of Chemistry Charlottesville, Virginia 22901	1	Dr. M. H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401	1
Dr. M. Tsutsui Texas A&M University Department of Chemistry College Station, Texas 77843	1	Dr. B. Foxman Brandeis University Department of Chemistry Waltham, Massachusetts 02154	1
Dr. M. F. Hawthorne University of California Department of Chemistry Los Angeles, California 90024	1	Dr. T. Marks Northwestern University Department of Chemistry Evanston, Illinois 60201	1
Dr. D. B. Brown University of Vermont Department of Chemistry Burlington, Vermont 05401	1	Dr. G. Geoffrey Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. W. B. Fox Naval Research Laboratory Chemistry Division Code 6130 Washington, D.C. 20375	1	Dr. J. Zuckerman University of Oklahoma Department of Chemistry Norman, Oklahoma 73019	1
Dr. J. Adcock University of Tennessee Department of Chemistry Knoxville, Tennessee 39716	1	Professor O. T. Beachley Department of Chemistry State University of New York Buffalo, New York 14214	1
Dr. W. Hatfield University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1	Professor P. S. Skell Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. D. Seyferth Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1	Professor K. M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167	1